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Structure of $SiSe_2$ based glasses

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Abstract

The structure of $(1-x)$ $SiSe_2$ – x Li_2Se glasses is examined by using a thermostatistical model of agglomeration. Singular solutions obtained from a time dependent equation of the model involving the probabilities of local structures are identified with the composition of the corresponding glass. This yields the dependence on x of the glass transition temperature and the existence of the Li_2SiSe_3 phase which are in good agreement with known experimental evidence. The model also gives the first numerical evaluation of the microstructural functions $E^{(n)}Q^{(k)}$, which correspond to typical medium-range structures.

1. Introduction

Sodium or lithium based chalcogenide glasses have received considerable attention during the past decade since it has been observed that they can produce high electrical conductivity. Among these glassy systems, lithium selenosilicates $x\,Li_2-(1-x)\,SiSe_2$ are of particular interest due to their well-known basic structure and that their structural and electrical study are generally related [1].

The structural properties change with the concentration of the modifier Li_2Se: long parallel chains of edge-sharing tetrahedra $SiSe_{4/2}$ which exist in the basic $SiSe_2$ glass and whose structure is close to that of the crystal of the same composition, disappear with the addition of the modifier. The chains are progressively broken and small isolated lithium-rich entities are expected [2–4], as observed in Raman and NMR spectroscopy.

2. Application of a statistical model of agglomeration

In this article, the application of a statistical agglomeration model [5] is performed on the $SiSe_2$–Li_2Se glass. This model, which is intended to describe the medium-range structure of crystalline and amorphous solids, is based mainly on the study of the critical size of an agglomeration process. Similar applications of the model have given a precise description of the structural properties of borate [6], thioborate [7] and lithium silicon sulphide systems [8]. As previously, the agglomeration into the doublets and triplets of elementary building blocks referred to as *singlets* (corresponding to the short range order in the glass) is modelled and their statistical contributions computed. The singlets should represent stable and rigid geometrical entities, derived from experimental observation. The $SiSe_4$ tetrahedra seem to match remarkably well this preliminary condition [9].

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The progressive addition of lithium ions leads to the destruction of the covalent Si–Se–Si bonds which exist between two neighbouring tetrahedra and produces the increasing number of ionic Si–$Se^{\ominus}Li^{\oplus}$ bonds instead. These selenium atoms bridged to a lithium cation are currently called non-bridging selenium atoms (NBS) because they do not relate to other Si-clusters upon increasing the Li_2Se molar fraction x. In an elementary $SiSe_4$ tetrahedron, we can expect therefore, respectively, zero, one, two or three non-bridging selenium atoms (whose corresponding NMR notation is $Q^{(4)}$, $Q^{(3)}$, $Q^{(2)}$ and $Q^{(1)}$ [10]). This will define our local configurations (singlets) used for the construction of multiplets which can be used over a wide range of x (configurations A, B, C and D). We assign to each of them an initial probability denoted by $P_A^{(0)}$, $P_B^{(0)}$, $P_C^{(0)}$ and $P_D^{(0)}$, respectively (see Fig. 1).

A fifth configuration E with four non-bridging selenium atoms (a tetrahedron with four $Se^{\ominus}Li^{\oplus}$ bond, i.e. the $Q^{(0)}$ structure) is excluded from our consideration. It yields trivial solutions in the forthcoming equations and it does not participate in the agglomeration process, because it does not involve covalent bonds, and does not appear in practice until $x = 0.66$ [11]. We assume therefore that the absence of this configuration does not affect the predictions of the model for low amounts of modifier.

It seems obvious that we can construct the whole vitreous matrix structure for every molar fraction $x < 0.66$ with these elementary singlets and that their probability is going to vary as function of x. This would represent at least a first level of approximation. With a second and better approximation the vitreous matrix structure should be constructed with more larger units, such as doublets, which are obtained during a *first step of agglomeration* from the joining of two singlets (A + A, A + B, A + C, etc.). These doublets whose number is, of course, greater than four may appear with a new probability which should take into account the initial probabilities $P_i^{(0)}$, the number of ways to obtain a same doublet (statistical weight) and an energetic factor (Fig. 2). It is now possible to produce typical substructures of the glass such as four and six-membered rings. The same construction can then be realized again in order to produce triplets (Fig. 3) by looking at all possible combinations of the singlets with the previous obtained doublets.

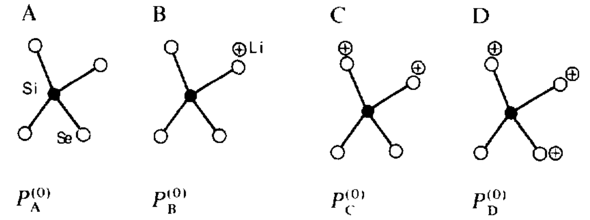


Fig. 1. The four elementary configurations with their initial probabilities.

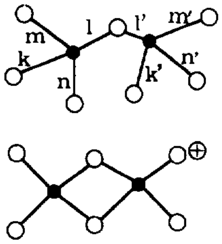
The existence of two ways of assembling the elementary tetrahedra leads to the introduction of two energetic factors e_1 and e_2 which are used in the computation of new probabilities after each agglomeration step. They depend on the binding energies between two tetrahedra and can be identified with a Boltzmann factor $e_i = \exp[-a_i/kT]$ when the process is realized in the vicinity of thermodynamical equilibrium. Our process is carried out during the annealing of the overcooled liquid where the factors e_i are probably still very close to the Boltzmann factors. Anyhow, even for supercooled liquids the use of Boltzmann factors gives a satisfactory description [12]. If two tetrahedra have a common edge (a situation common for small values of x), the probability of such a doublet will be multiplied by the factor e_2; if two tetrahedra have a common corner (at bigger values of x), the probability will be multiplied by e_1. We shall be able to evaluate the new probabilities of doublets and triplets during the agglomeration process in terms of $P_A^{(0)}$, $P_B^{(0)}$, $P_C^{(0)}$ and $P_D^{(0)}$.

Now, one can write the new probabilities, taking into account the number of ways W_{ij}^m ($m = 1$ for corner-sharing doublets and $m = 2$ for edge-sharing ones) which lead to the same doublet from two singlets i and j whose probabilities are $P_i^{(0)}$ and $P_j^{(0)}$ respectively:

$$P_{ij(m)}^{(1)} = \frac{1}{Q_1} W_{ij}^{m} P_i^{(0)} P_j^{(0)} e^{-a_m/kT}, \qquad (1)$$

where Q_1 is the normalizing factor which assures that the sum of all $P_{ij}^{(1)}$ is equal to 1. One can produce 16 doublets during the first step; two of them are displayed in Fig. 2 with their corresponding probabilities.

The agglomeration process is performed in the same manner for the second step [60 triplets with



$P^{(1)}_{\mathrm{AA}(1)} = \frac{1}{Q_1} 16\, P^{(0)^2}_{\mathrm{A}}\, \mathrm{e}^{\;a1/kT}$ corner-sharing (A + A) doublet (one (Si–Se–Si bond)

$P^{(1)}_{\mathrm{AB}(2)} = \frac{1}{Q_1} 36\, P^{(0)^2}_{\mathrm{A}}\, P^{(0)}_{\mathrm{B}} \mathrm{e}^{-a2/kT}$ edge-sharing (A + B) doublet (two (Si–Se–Si bonds)

Fig. 2. Two doublets, a corner-sharing A–A and an edge-sharing A–B doublet with their corresponding probability. With labelled Si–Se bridges, there are 16 different ways to obtain the same doublet AA1 (*l*–*l*′, *l*–*m*′, *l*–*n*′, etc.) which gives the statistical weight $W_{\mathrm{AA1}} = 16$.

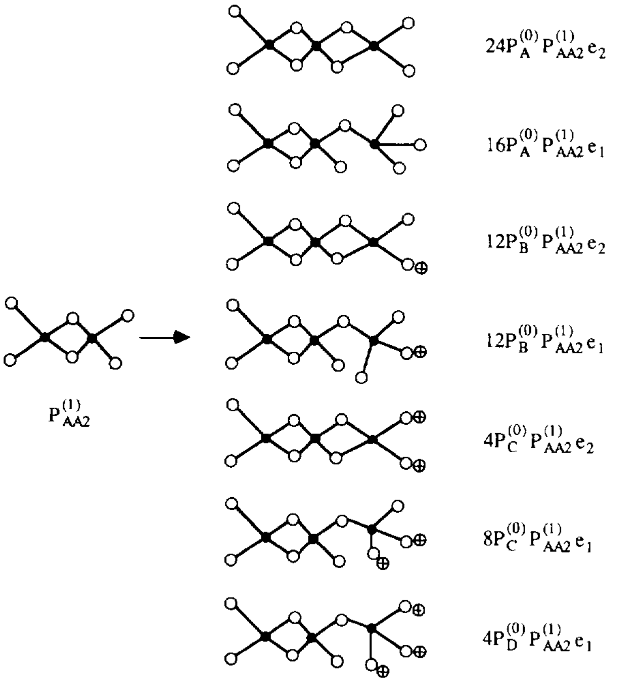


Fig. 3. From the doublet AA2 to a set of triplets.

probability $P^{(2)}_{ijl(m)}$ $(i,j,l = \mathrm{A,B,C,D};\quad m = 1,2)$ (Fig. 3)]. At each step, we compute the new relative probabilities corresponding to the four elementary configurations, for example

$$P^{(1)}_i = \frac{1}{2}\left[2P^{(1)}_{ii} + \sum_{j \neq i} P^{(1)}_{ij}\right] \tag{2}$$

for the first step. One may note that the SiSe$_2$ based glass has the same statistics as the lithium silicon sulphide glass [8] which can be considered as a structural explanation of their similar properties.

Let us define a function $s(t)$ chosen between two well-defined limits in order to deduce a time dependent equation for the probabilities [5, 13]. The parameter $s(t)$ corresponds roughly to the number of steps realized $(0 < s(t) < 1$ for the first one, $1 < s(t) < 2$ for the second one, etc.) and also evaluates the approximate density of multiplets already formed. During the kth step of agglomeration $(k - 1 < s < k$ with $k > 0)$, we shall evaluate the approximate probability of finding the ith elementary configuration $(i = \mathrm{A,B,C,D})$ as follows:

$$P_i(t,T) = (k-1)\left[\frac{s(t)}{k-1} - 1\right] P^{(k)}_i + k\left[1 - \frac{s(t)}{k}\right] P^{(k-1)}_i, \tag{3}$$

where $P^{(k)}_i$ is the relative probability of an i-singlet at the kth step. For $0 < k < 1$, we have

$$P_i(t,T) = s(t)P^{(1)}_i + [1 - s(t)]P^{(0)}_i. \tag{4}$$

The probability $P^{(k)}_i$ is always normalized by the factor Q_k in order to keep the sum of the probabilities equal to 1 at each step:

$$Q_k = P^{(k)}_{\mathrm{A}} + P^{(k)}_{\mathrm{B}} + P^{(k)}_{\mathrm{C}} + P^{(k)}_{\mathrm{D}}. \tag{5}$$

The derivative with respect to t of Eq. (3) can be easily obtained and leads to a system of three equations with three independent variables $P^{(0)}_i$. The relative probability of an elementary configuration should not vary from one step to another because we have assumed that the vitreous matrix can be tiled with multiplets of different sizes, yielding at each time a better approximation of the structure (Fig. 4):

$$\frac{\mathrm{d}P_i(t,T)}{\mathrm{d}t} = \frac{\mathrm{d}s}{\mathrm{d}t}\frac{\mathrm{d}P_i(t,T)}{\mathrm{d}s} = \frac{\mathrm{d}s}{\mathrm{d}t}[P^{(k)}_i - P^{(k-1)}_i] = 0. \tag{6}$$

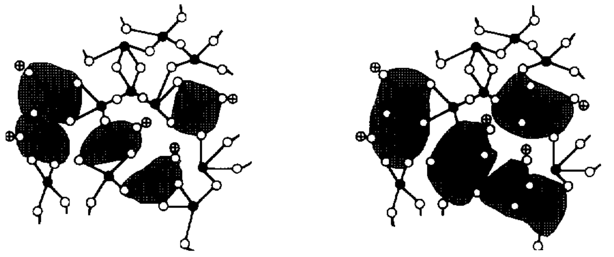


Fig. 4. A schematic representation of a lithium selenosilicate network. For $k = 1$, one assumes that it is equivalent to tile the network with singlets $[P_{\mathrm{B}}^{(0)}]$ or with doublets $[P_{i\mathrm{B}}^{(1)}]$ (shaded regions), giving a graphical illustration for one of the equations of the system (6). The same happens for the A, C and D configurations, which explains that there are also unshaded regions on this figure.

Nevertheless, it seems also necessary to introduce a cooling term in Eq. (6) because lithium based SiSe_2 glasses are mainly obtained by fast quenching techniques involving very high cooling rates ($10^6\ \mathrm{K\,s^{-1}}$ [3, 14]), so that $\mathrm{d}T/\mathrm{d}t$ becomes non-negligible. A new term has to be added into the right-hand side of Eq. (6) (this means that d Log $T/\mathrm{d}t$ has at least the same order of magnitude as $\mathrm{d}s/\mathrm{d}t$) [5]:

$$\frac{\mathrm{d}P_i(t,T)}{\mathrm{d}t} = \frac{\mathrm{d}s}{\mathrm{d}t}\left[P_i^{(k)} - P_i^{(k-1)}\right] + \frac{\mathrm{d}T}{\mathrm{d}t}\frac{\partial P_i^{(k)}}{\partial T} = 0. \quad (7)$$

With the four elementary configurations A, B, C and D, this leads to a set of three independent equations with three variables $P_i^{(0)}$ (with $k = 1$ for the first step and $k = 2$ for the second one):

$$P_{\mathrm{A}}^{(k)} - P_{\mathrm{A}}^{(k-1)} - \frac{|\mathrm{d}T/\mathrm{d}t|}{\mathrm{d}s/\mathrm{d}t}\frac{\partial P_{\mathrm{A}}^{(k)}}{\partial T} = 0,$$

$$P_{\mathrm{B}}^{(k)} - P_{\mathrm{B}}^{(k-1)} - \frac{|\mathrm{d}T/\mathrm{d}t|}{\mathrm{d}s/\mathrm{d}t}\frac{\partial P_{\mathrm{B}}^{(k)}}{\partial T} = 0,$$

$$P_{\mathrm{C}}^{(k)} - P_{\mathrm{C}}^{(k-1)} - \frac{|\mathrm{d}T/\mathrm{d}t|}{\mathrm{d}s/\mathrm{d}t}\frac{\partial P_{\mathrm{C}}^{(k)}}{\partial T} = 0. \quad (8)$$

We shall identify the singular solutions of this new system with a metastable state describing the statistical properties of the glass [5].

We can still reduce the number of independent equations by taking into account the fact that the molar fraction x is expressed as follows:

$$\frac{x}{x-1} = \tfrac{1}{2}[P_{\mathrm{B}}^{(0)} + 2P_{\mathrm{C}}^{(0)} + 3P_{\mathrm{D}}^{(0)}]$$

$$= \tfrac{1}{2}[3 - 3P_{\mathrm{A}}^{(0)} - 2P_{\mathrm{B}}^{(0)} - P_{\mathrm{C}}^{(0)}]. \quad (9)$$

Relation (9) can be interpreted as the equation for charge conservation, i.e. the sum of all positive charges ($\mathrm{Li}^{\oplus}$) must be equal to the sum of the negative ones which exist on the local configurations [15].

This will reduce system (8) to a set of two independent equations, with two independent variables $P_i^{(0)}$.

3. Results and discussion

As for the previous applications of the model [6–8], we solve the reduced system (8) for both steps by a computer program based on the generalized Newton method. We start with approximate values of the binding energies a_1 and a_2 which are probably very close to those found in thiosilicate glasses [11]. The solutions will be contained in a symplex defined by: $0 \leqslant P_{\mathrm{A}}^{(0)} \leqslant 1$, $0 \leqslant P_{\mathrm{B}}^{(0)} \leqslant 1$, $0 \leqslant P_{\mathrm{C}}^{(0)} \leqslant 1$, $0 \leqslant 1 - P_{\mathrm{A}}^{(0)} - P_{\mathrm{B}}^{(0)} - P_{\mathrm{C}}^{(0)} \leqslant 1$ and lying on the plane:

$$3 - 3P_{\mathrm{A}}^{(0)} - 2P_{\mathrm{B}}^{(0)} - P_{\mathrm{C}}^{(0)} = 2\frac{x}{1-x}. \quad (10)$$

Solutions which exist at the borders of this domain will be identified with crystalline structures (i.e. when $P_{\mathrm{B}}^{(0)} = 1$ we should have diselenosilicates, $P_{\mathrm{C}}^{(0)} = 1$ metaselenosilicates and $P_{\mathrm{D}}^{(0)} = 1$ pyroselenosilicates), whereas the solutions inside the symplex will represent the glassy state because of their meta-stable character and for the fact that they represent a mixture of all possible configurations, which corresponds to a maximum of the configurational entropy.

With this in mind, we can start the investigation of the system by systematically scanning a reasonable domain of variation of the parameters a_1, a_2 and the temperature T. Although the change from supercooled liquid to glass does not take place at a well-defined temperature and depends on the glass preparation and on the cooling rate [1], we shall fit the factor Λ, defined by

$$\Lambda = \frac{\mathrm{d}T/\mathrm{d}t}{T\,\mathrm{d}s/\mathrm{d}t}, \quad (11)$$

which is obtained by computing Eqs. (8), in order to identify the first solution which appears during a temperature scanning with the glass transition temperature obtained by Michel-Lledos and coworkers [2] (see Table 1).

This is the most explicit constraint we have to satisfy with given input (a_1, a_2, Λ). The probability

Table 1
The experimental values of T_g [in °C] for different concentrations of modifier, obtained by Michel-Lledos and co-workers [2]

x	0.2	0.3	0.35	0.4	0.45	0.5	0.6
T_g	284	277	276	291	276	272	251

of finding the A, B, C and D configurations can vary indeed with respect to the temperature during the quenching of the liquid. This variation should stop at the glass transition temperature (when the liquid gets frozen), so that the lower limit of the temperature range in which we find solutions for the reduced system (8) can be clearly identified with T_g.

Testing this experimental constraint by an iterative method, we obtain the best fits for both steps for

$$a_1 = 0.20\,\text{eV}, \tag{12}$$

$$a_2 = 0.32\,\text{eV}. \tag{13}$$

These values are in good agreement with those usually proposed in the $SiSe_2$ glasses by numerical computation [16]. The best fits of the cooling factor Λ are displayed in Fig. 5.

The glass transition temperature agrees quite well with the experimental data for both steps and depends, as in the experiments, on the cooling rate, represented by Λ (Tables 1 and 2). The spurious value of T_g at $x = 0.6$ can possibly be explained by the fact that the $Q^{(0)}$ configuration (a tetrahedron with four $Se^{\ominus}Li^{\oplus}$ bonds) becomes non-negligible. Anyhow, this solution is obtained with a very low cooling factor, which does not seem to be consistent with observation.

The first step of agglomeration yields a solution with high A and C probabilities. This is identified with a mixture of the progressive vanishing $SiSe_2$ glass (large A concentration) and the Li_2SiSe_3 species with large amounts of the configuration C (Fig. 6). The roughest approximation which is represented here by the first step seems to describe the most important structural change with x in the system $(1 - x)\ SiSe_2 - x\ Li_2Se$. Indeed, the main structural effects induced by the modifier in the selenosilicate glasses for $0 \leqslant x \leqslant 0.5$ are the destruction of the network former and the progressive apparition of the metaselenosilicate phase [4]. These two behaviours are predicted by the first step (Table 2).

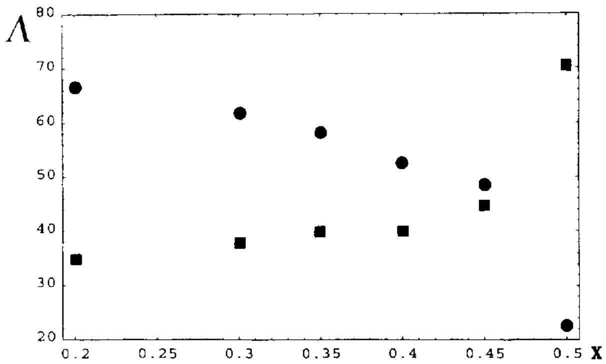


Fig. 5. The cooling factor Λ obtained for the first (circles) and second step (squares).

Table 2
The predicted glass transition temperature [in °C] and the corresponding solutions of the reduced system (8) for the first (I) and second step (II) of agglomeration

x	T_g	$P_A^{(0)}$	$P_B^{(0)}$	$P_C^{(0)}$	$P_D^{(0)}$
0.2	284 (I)	0.750	0.008	0.234	0.008
	284 (II)	0.715	0.096	0.163	0.026
0.3	277 (I)	0.580	0.031	0.339	0.049
	277 (II)	0.529	0.158	0.241	0.073
0.35	276 (I)	0.477	0.039	0.415	0.069
	276 (II)	0.489	0.162	0.132	0.217
0.4	291 (I)	0.369	0.056	0.446	0.128
	291 (II)	0.305	0.260	0.231	0.204
0.45	276 (I)	0.259	0.073	0.439	0.228
	276 (II)	0.189	0.315	0.167	0.329
0.5	272 (I)	0.000	0.000	0.998	0.001
	272 (II)	0.099	0.243	0.218	0.440
0.6	56 (I)	0.002	0.002	0.002	0.994

At $x = 0.5$, one has a pure phase composed of a partially ordered network. At this concentration, the solution of the reduced system (8) is composed mainly of C-configurations ($P_C^{(0)} = 0.998$), which corresponds to a Li_2SiSe_3 phase with polymeric corner-sharing C–C doublets. The probability of this doublet is about 95%. The cooling factor Λ decreases from $x = 0.2$ to $x = 0.5$ and is in close correspondance with the experimental quenching rate which is necessary to form the glass [17].

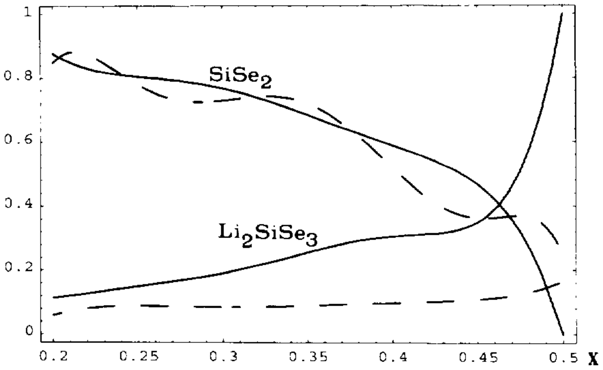


Fig. 6. The probability of finding the $SiSe_4$ and Li_2SiSe_3 phase for the first (solid line) and second step of agglomeration (dashed line).

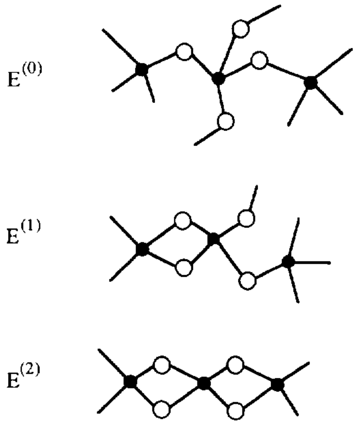


Fig. 7. Definition of the microstructure functions $E^{(n)}$.

Table 3
The observed microstructure functions $E^{(n)}Q^{(k)}$ and the evaluation proposed by the first and second step of the model

x	Observed microstructural functions [4]	Corresponding probability	
		First step	Second step
0.2	$E^{(0)}Q^{(3)}$		5.8%
	$E^{(0)}Q^{(2)}$	10.3%	6.0%
	$E^{(1)}Q^{(3)}$		1.4%
	$E^{(1)}Q^{(4)}$	36.1%	27.8%
	$E^{(2)}Q^{(4)}$	3.1%	0.8%
0.35	$E^{(0)}Q^{(3)}$	4.6%	13.0%
	$E^{(0)}Q^{(2)}$	15.1%	6.0%
	$E^{(1)}Q^{(3)}$	1.6%	2.7%
	$E^{(1)}Q^{(4)}$	27.7%	22.0%
0.45	$E^{(1)}Q^{(3)}$	1.7%	4.9%
	$E^{(0)}Q^{(2)}$	39.6%	9.8%
0.5	$E^{(0)}Q^{(2)}$	94.8%	16.8%
0.6	$E^{(0)}Q^{(2)}$		
	$E^{(0)}Q^{(1)}$	99.9%	

At $x = 0.6$, we obtain a pure $Li_6Si_2Se_7$ phase ($P_D^{(0)} \sim 1$, pyroselenosilicates), which is in close agreement with the proposal of Pradel and coworkers suggested by ^{29}Si NMR spectroscopy [4].

The second step gives another insight of the structural change in the glass. In addition to the main behaviour as the decrease of the A-configuration and the growth of the Li_2SiSe_3 phase (Fig. 6), one obtains the solution with non-negligible rates of B and D configurations, corresponding to the $Q^{(3)}$ species for $0.2 \leqslant x \leqslant 0.45$ (Table 2). There is no solution for $x = 0.6$, the triplet approximation is no more significant at this concentration because the vitreous matrix is composed mainly of non-bridging doublets (D–D, pyroselenosilicates) and $Q^{(0)}$ singlets.

The structural change in the lithium silicon selenide glass can be interpreted more precisely in terms of microstructural functions $E^{(n)}Q^{(k)}$ [3]. Indeed, the existence of the $E^{(n)}$ functions [$n = 0$, two Si–Se–Si bonds per tetrahedron $SiSe_4$; $n = 1$, three Si–Se–Si bonds; $n = 2$, four Si–Se–Si bonds (Fig. 7)] depends on the concentration x (one expects more and more $E^{(0)}$ functions with growing x) These functions can be easily computed by use of the probability of doublets and triplets (Figs. 2 and 3) taking into account the solution $P_i^{(0)}$ (Table 2). The most significant results are displayed in Table 3 and related to the experimental observed ones.

The table shows that the edge-sharing destruction is very rapid, i.e. the $E^{(2)}Q^{(4)}$ function has become already negligible at $x = 0.2$, the decrease of the $E^{(1)}Q^{(4)}$ structure is also comparable with the general observation [4]. The $E^{(0)}Q^{(3)}$ and $E^{(1)}Q^{(3)}$ functions exist until $x \sim 0.45$. The growing proportion of the $E^{(0)}Q^{(2)}$ is consistent with the increase of the Li_2SiSe_3 phase which is composed only of polymeric corner-sharing tetrahedra whereas the dimeric edge-sharing tetrahedra (a $E^{(1)}Q^{(2)}$ structure), which exist with a rate of 25% in the sulphide analogue glass [3], has a probability of less than 4% at $x = 0.5$ in the selenide system. However, the two steps show the general increase of the $E^{(0)}$ functions with x, i.e. the conversion of edge-sharing tetrahedra into corner-sharing tetrahedra ($E^{(2)} \rightarrow E^{(1)} \rightarrow E^{(0)}$). The numerical results on the microstructure functions are in good agreement with the experimental NMR observation of Pradel and co-workers [4]. Each step describes more precisely particular features of the structural change ($Q^{(4)} \rightarrow Q^{(2)}$ conversion for the first step and the same conversion and the existence of $Q^{(3)}$ species for the second step).

4. Summary and conclusion

The statistical model of agglomeration works quite well here and shows, as in the previous articles, several important results for the theoretical description of the medium-range structure of $(1-x)\ SiSe_2 - x\ Li_2Se$ systems. The results depend only upon two independent parameters ($a_2 - a_1$, A). Indeed, the model principaly uses the energy differences, because all the probabilities are normalized by the Q_k factors. With these two parameters, we have been able to show that:

(1) The first step describes the main structural change of the system which is the vanishing of the network former and the growth of the Li_2SiSe_3 phase.

(2) The second step gives a more precise insight of the structural change by predicting the existence of $Q^{(3)}$ species and its mixture with the other $Q^{(k)}$ compounds.

(3) The exact dependence of the glass transition temperature on x is obtained for both steps of agglomeration. With the first step, the variation of the cooling factor A with x is very close to the one necessary to obtain the glass.

(4) The observed microstructural functions $E^{(n)}Q^{(k)}$ can be evaluated very easily with the probability of multiplets.

These encouraging results may be used in the future for the study of related systems such as the sodium or silver selenium sulphide, or the investigation of interesting physical properties of these glasses like density and conductivity.

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